CLAIMS

22. (previously added) A process for the preparation of a nitro-substituted aromatic carboxylic acid ester comprising the step of:

reacting a nitro-substituted aryl halide, in the absence of water and oxygen, with carbon monoxide and an alcohol in the presence of a metal catalyst and a proton acceptor to form a corresponding nitro-substituted aromatic carboxylic acid ester,

wherein:

said aryl group of said nitro-substituted aryl halide is a substituted or unsubstituted, monocyclic or polycyclic aryl group or heteroaryl group containing at least one heteroatom of N, O, or S;

said carbon monoxide is present at a pressure of 14.7- 1100 psi;

said alcohol is a linear or branched, substituted or unsubstituted C_1-C_5 alkyl alcohol;

said proton acceptor is a tertiary amine base; and

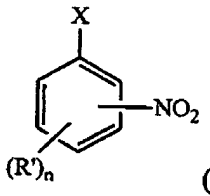
said metal catalyst is a heterogeneous catalyst of palladium metal deposited on activated carbon present in an amount of between about 1 weight percent and 500 weight percent based on said nitro-substituted aryl halide.

23. (previously added) A process of claim 22, wherein said tertiary amine base is selected from the group consisting of triethylamine and tri-n-butylamine.

24. (previously added) A process of claim 22, wherein

said reacting step occurs in the presence of a solvent selected from the group consisting of an excess of said alcohol, an excess of said proton acceptor, an aliphatic hydrocarbon, an aromatic hydrocarbon, a cyclic ether, an acyclic ether, a polar aprotic solvent, and mixtures thereof.

25. (previously added) A process of claim 22, wherein said nitro-substituted aryl halide is of formula (I):



(I)

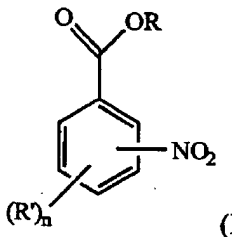
wherein

X is chloro, bromo, or iodo;

n is an integer of 1-4;

each RN is, independently, a C_1-C_{10} alkyl group, a C_2-C_{10} alkenyl group, a C_2-C_{10} alkynyl group, a C_4-C_{10} aryl or heteroaryl group, an ether, a thioether, a nitro, a trifluoromethyl, a fluoro, cyano, or acyl group; or together with the phenyl ring forms a substituted or unsubstituted fused polycyclic ring system; and

said corresponding nitro-substituted aromatic carboxylic acid ester is of formula (II):



(II)

wherein

n and RN are as defined above; and

R is a C_1-C_5 alkyl group.

26. (previously added) A process of claim 25, wherein n is 1, RN is a trifluoromethyl group, and R is a methyl or n-butyl group.

27. (previously added) A process of claim 26, wherein RN is para to halide X of formula (I) and the nitro group is ortho to halide X of formula (I).

28. (previously added) A process for the preparation of a thioether-substituted aromatic carboxylic acid ester comprising the steps of:

preparing a nitro-substituted aromatic carboxylic acid ester according to claim 22, and

reacting the said nitro-substituted aromatic carboxylic acid ester with a thiolate anion to form the corresponding thioether-substituted aromatic carboxylic acid ester.

29. (previously added) A process of claim 28, wherein said thiolate anion is prepared *in situ* from a thiol and a base, wherein

said base is selected from the group consisting of tertiary amines, alkali or alkaline earth metal hydroxides, and alkali or alkaline earth metal carbonates.

30. (previously added) A process of claim 29, wherein said thiolate anion is a compound of the formula ROS^-M^+, wherein

RO is a C_1-C_{10} alkyl group or a C_4-C_{10} aryl or heteroaryl group; and

M is selected from the group consisting of sodium, potassium and ammonium.

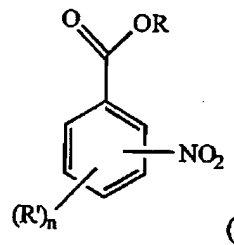
31. (previously added) A process of claim 28, wherein said reacting step is conducted in a homogeneous solvent system comprising a water-miscible solvent and water, or in a phase-transfer solvent system comprising a water-immiscible organic solvent, a phase-transfer catalyst, and, optionally, water.

32. (previously added) A process of claim 31, wherein said reacting step is conducted in a phase-transfer solvent system wherein

said phase-transfer catalyst is a tetralkylammonium or tetralkylphosphonium salt selected from the group consisting of tetrabutylammonium bromide, tetrabutylammonium chloride, methyltributylammonium chloride, methyl trioctylammonium chloride, and tetrabutylphosphonium bromide; and

said water-immiscible solvent is selected from the group consisting of an aliphatic hydrocarbon, an aromatic hydrocarbon, a cyclic ether, and an acyclic ether.

33. (previously added) A process of claim 30, wherein said nitro-substituted aromatic carboxylic acid ester is of formula (II):



(II)

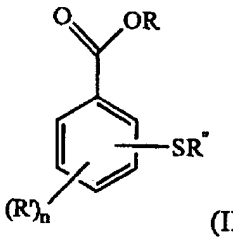
wherein

n is an integer of 1-4;

each RN is, independently, a C_1-C_{10} alkyl group, a C_2-C_{10} alkenyl group, a C_2-C_{10} alkynyl group, a C_4-C_{10} aryl or heteroaryl group, an ether, a thioether, a nitro, a trifluoromethyl, a fluoro, cyano, or acyl group; or together with the phenyl ring forms a substituted or unsubstituted fused polycyclic ring system; and

R is a C_1-C_5 alkyl group; and

said corresponding thioether-substituted aromatic carboxylic acid ester is of formula (III):



(III)

wherein

n, RN, and R are as defined above; and

RO is a C_1-C_{10} alkyl group or a C_4-C_{10} aryl or heteroaryl group.

34. (previously added) A process of claim 33, wherein RN is para to the ester group of formula (II) and the nitro group is ortho to the ester group of formula (II).

35. (previously added) A one-pot process for the preparation of a thioether-substituted aromatic carboxylic acid ester comprising the steps of:

reacting a nitro-substituted aryl halide, in the absence of water and oxygen, with carbon monoxide and an alcohol in the presence of a metal catalyst and a proton acceptor to form the corresponding nitro-substituted aromatic carboxylic acid ester,

wherein:

said aryl group of said nitro-substituted aryl halide is a substituted or unsubstituted, monocyclic or polycyclic aryl group or heteroaryl group containing at least one heteroatom of N, O, or S;

said carbon monoxide is present at a pressure of 14.7- 1100 psi;

said alcohol is a linear or branched, substituted or unsubstituted C_1-C_5 alkyl alcohol;

said proton acceptor is a tertiary amine base; and

said metal catalyst is a heterogeneous catalyst of palladium metal deposited on activated carbon present in an amount of between about 1 weight percent and 500 weight percent based on said nitro-substituted aryl halide, and

reacting without isolating said corresponding nitro-substituted aromatic carboxylic acid ester with a thiolate anion to form the corresponding thioether-substituted aromatic carboxylic acid ester.